

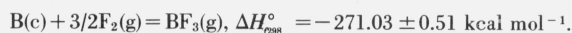
The Heat of Formation of Boron Trifluoride by Direct Combination of the Elements¹

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The energy of combination of crystalline boron in gaseous fluorine was measured in a bomb calorimeter. The experimental data combined with reasonable estimates of all known errors may be expressed by the equation:



This result is compared with other recent work on and related to the heat of formation of boron trifluoride.

Key Words: Bomb calorimeter, boron, boron trifluoride, fluorine, heat of formation, Teflon.

1. Introduction

An accurate value for the heat of formation of boron trifluoride is of significant importance because this value is involved in the thermochemistry of many boron compounds. The study of the thermochemistry of boron compounds was for a long time hampered by difficulties in measuring a suitable reaction involving elemental boron. The heat of formation of boric oxide, for instance, was uncertain to several kilocalories per mole because of the difficulty of getting complete combustion of the element in oxygen, or of determining the amount of reaction, in the absence of complete combustion. The difficulty was apparently due to the glassy and nonvolatile character of the boric oxide formed, which tended to terminate the reaction before completion, and made the analysis of the product a complex problem.

The thermochemistry of boron was placed on a firm basis by the work of Prosen, Johnson, and Pergiel [1, 2]² on the decomposition and hydrolysis of diborane, and of Johnson, Miller, and Prosen [3] on the heat of formation of boron trichloride from the elements. With the aid of the heats of these reactions and other data, they obtained reasonably consistent values for $\text{B}_2\text{O}_3(\text{c})$, $\text{H}_3\text{BO}_3(\text{c})$, $\text{B}_2\text{H}_6(\text{g})$, and $\text{BCl}_3(\text{g})$. While more recent work has suggested changes in some of the values, these changes have been small.

The heat associated with the direct combination of the elements in a bomb calorimeter was measured by Wise, Margrave, Feder, and Hubbard [4], who found the heat of formation of $\text{BF}_3(\text{g})$ to be $-269.88 \pm 0.24 \text{ kcal mol}^{-1}$. Another study involving the direct combination of the elements by Gross, Hayman, Levi, and Stuart [5] gave $-271.20 \text{ kcal mol}^{-1}$ for the heat of formation of $\text{BF}_3(\text{g})$.

More recent additional measurements by Johnson, Feder, and Hubbard [6] showed that the calorimetric work of Wise et al. [4], was correct, but reanalysis of the boron sample revealed impurities not previously taken into account. A recalculation of their earlier data gave for $\Delta H_{f298}^\circ [\text{BF}_3(\text{g})]$, $-271.6 \pm 0.9 \text{ kcal mol}^{-1}$. The calorimetric measurements reported by Johnson et al. [6], were made using a boron sample of greater purity in both a conventional-type combustion bomb and a two-chambered combustion bomb and led to a value for $\Delta H_{f298}^\circ [\text{BF}_3(\text{g})]$ of $-271.65 \pm 0.22 \text{ kcal mol}^{-1}$.

Research prior to the work of Wise et al. [4], is neither sufficiently detailed nor accurate enough to derive a value for the heat of formation of BF_3 having an uncertainty less than several kilocalories per mole, and hence, has not been considered. Gmelin [7] provides a review of the earlier work on this subject for the interested reader.

We felt that additional confirmatory work on the heat of formation of BF_3 was needed to establish more fully the recent work of Gross et al. [5], and Johnson et al. [6]. In addition, we have found that work in our laboratory on the measurement of the heats of combustion of several refractory boron compounds has produced values for their heats of formation very

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² Figures in brackets indicate the literature references at the end of this paper.

sensitive to the auxiliary value used for the heat of formation of boron trifluoride. Some systematic errors in the calculated heats of formation may be avoided by measuring the heat of combustion of boron using a similar procedure in the same apparatus. The variations in the heat of formation of BF_3 , as reported by other investigators, are large enough to make a significant difference in the heats of formation of metallic borides if calculated from their heats of combustion in fluorine.

2. Materials

2.1. Boron

The sample of β -rhombohedral boron was obtained from the Eagle-Picher Company and had been prepared by the hydrogen reduction of boron tribromide on a substrate of zone refined boron. The maximum particle size was $150\ \mu$. The supplier reported traces of copper and silicon and a small amount of carbon in the sample. The sample was analyzed spectrographically for metallic impurities and quantitatively

for individual metals to 0.001 percent. A nitrogen assay was made using the Kjeldahl method and the carbon content was determined by oxygen combustion of the sample and measurement of the CO_2 formed. This measurement gave a higher carbon content than was indicated by the supplier. We preferred our carbon analysis for the assay of our sample. The analysis for oxygen in our boron sample was performed by both neutron activation and inert-gas fusion methods. The oxygen analysis obtained by inert-gas fusion is preferred over the analysis by neutron activation because of suspected interference by isotopic species produced from irradiation of the boron itself [8]. Table 1 summarizes the analysis of the boron sample, showing the total boron content to be 99.68 percent by difference.

An x-ray diffraction pattern of the boron sample determined by the NBS Crystallography Section yielded lattice parameters in good agreement with data reported earlier. The lattice parameters were $a = 10.922\ \text{\AA}$ and $c = 23.79\ \text{\AA}$ (compared to $a = 10.944\ \text{\AA}$ and $c = 23.811\ \text{\AA}$ [10]) and the space group found was $R\bar{3}m$.

TABLE 1. Analysis of the boron sample ^a

Metal impurities								Total
Al	Fe	Mg	Mn	Sr	Ca	Si	Cu	0.120
< 0.001	0.079	0.002	0.014	0.002	0.010	0.012 (0.0003) ^b (0.0007) ^b	
Nonmetallic impurities								
N		O			C		0.203	
< 0.005		0.088 ^c (0.161) ^d			0.11 (0.05) ^e			
Assumed presence of nonmetallic impurities								
BN		B ₂ O ₃			B ₄ C		99.677	0.643
0.009		0.128			0.506			
Total boron content.....								99.237
Total boron as the element.....								

^a Analyses presented in table 1 were performed by the NBS Analysis and Purification Section, unless otherwise stated.

^b Supplier's analysis (Eagle-Picher Co.).

^c Inert-gas fusion (Ledoux and Co.).

^d Neutron activation analysis (General Atomic).

^e Supplier's analysis for carbon in boron by the method of Kuo, Bender, and Walker [9].

2.2. Teflon (Polytetrafluoroethylene)

The Teflon film and Teflon powder ("Teflon 7") used in preparing pelleted mixtures for combustion experiments were the same as we have described in an earlier publication [11]. Here again neither the Teflon powder nor the Teflon film were modified or treated in any special way prior to use. The energy of combustion, ΔE_{303}° , of the Teflon (film and powder) was $-10,372.8 \text{ Jg}^{-1}$ [11].

The fluorine used in the heat measurements assayed at 99.40 percent F_2 . The fluorine was analyzed by absorbing the F_2 in mercury and observing the pressure and composition of the residual gases [12]. The composition of the residue was determined by examination in a mass spectrometer. Table 2 shows the results of typical analysis of a fluorine sample.

TABLE 2. Composition of fluorine sample

Constituent	Mole percent
F_2	^a 99.40
O_2	0.0960
N_2	.2784
CO_2	.0175
CF_4	.1962
Ar	.0083
SO_2F_2	.0001
SiF_4	.0003
C_2F_6	.0023
SF_6	.0001
C_4F_8	.0002
C_3F_8	.0005
C_2F_4 or cyclic C_4F_8	.0001

^a By difference.

3. Preparation of Sample Pellets

The first step of the procedure used to prepare the boron sample for combustion in fluorine was to mix the sample with Teflon powder in a bag made of Teflon film. The bagged mixture was then pelleted and provided with an additional coating of Teflon (method B of our earlier work [11]). Attempts to burn pelleted mixtures of boron and Teflon powder on which no outer Teflon coating was provided (method A, [11]) resulted in spontaneous combustion of the pellet during the fluorine-loading procedure. However, if method B was used, it was possible to carry out the calorimetric experiment, and the apparent heat transfer coefficients calculated for the calorimeter in these heat measurements were comparable to that of a normal combustion experiment in which no premature reaction was taking place.

Much care is needed in keeping track of the cumulative mass of the sample as the Teflon and boron are added because some losses are always observed and their distribution significantly affects the results of the experiment.

Table 3 gives average values for the amounts of Teflon and boron used in preparing a pellet and the losses detected in the process. The sample masses were adjusted for losses in the manner previously described [11].

The densities used for the Teflon film, Teflon powder, and boron in making buoyancy corrections were 2.15, 2.16, and 2.35 g cm^{-3} [13], respectively. Weighings of pelleted mixtures and intermediate stages were made to 0.01 mg.

TABLE 3. Amounts of sample and losses incurred during pellet preparation (averages)

1. Mass of Teflon bag.....g...	0.30
2. Mass of boron in mixture.....g...	.16
3. Mass of Teflon in mixture.....g...	1.88
4. Mass of Teflon coating.....g...	0.70
5. Loss of Teflon in sealing bag.....mg...	.32
6. Loss of mixture in pelleting.....mg...	.30
7. Total loss in preparation.....mg...	.62

4. Calorimetric System

No major changes had been made in the bomb calorimeter, thermometric system or combustion bomb since our earlier work [11] which was carried out with the same apparatus. The apparatus will be discussed here only briefly.

An isothermal-jacket, stirred-water calorimeter was used; the jacket was maintained at a constant temperature near 30°C within 0.002°C . Temperature changes in the calorimeter were measured to 0.0001°C with a G-2 Mueller bridge in conjunction with a platinum resistance thermometer. Reactions were carried out in an "A" nickel combustion bomb, designed for service with fluorine, having a volume of approximately 360 ml. Two aluminum electrodes each suspended from the bomb head by a monel rod held a tungsten fuse (0.002 inch diam) which contributed about 20 J to the combustion energy, assuming complete combustion. The quantities of boron and Teflon in the pellets were adjusted to produce a temperature rise in the calorimeter of about 3 deg (27 to 30°C). For procedures dealing with the loading and emptying of the combustion bomb, and for details of the design and construction of the fluorine manifold, our earlier work should be consulted [14].

5. Products of Combustion

Our previous work [11, 14] has established that Teflon burns in 15 to 21 atm of fluorine to carbon tetrafluoride as the only major product. Higher fluorocarbons were not detected in amounts greater than 0.02 mole percent. The product gases were analyzed in a mass spectrometer after absorption of the excess fluorine in mercury. It is interesting to note that the mass spectrometric examination of product gases from a boron-Teflon combustion experiment showed no sign of BF_3 . We suspect that under the conditions of the reaction of fluorine with mercury, an interaction of some kind takes place between BF_3 and the mercury fluoride formed during the absorption of fluorine.

A typical analysis of the residual product gases from a combustion experiment is shown in table 4. The amounts of minor constituents found in the product

gases are greater than those expected on the basis of the amounts present as impurities in the original fluorine. The increments observed in the minor constituents were probably introduced during sampling and analysis procedures and were probably not involved in the actual bomb process.

Boron trifluoride was identified as a combustion product by infrared spectrometry. Examination in the region 650 to 400 cm^{-1} of a sample of the bomb product gases containing excess fluorine revealed the BF_3 band at 481 cm^{-1} and the CF_4 band at 630 cm^{-1} . Spectra of the evacuated cell and of BF_3 alone were taken over the region mentioned above to substantiate the identification. The cell used was 8 cm long and had polyethylene windows, 0.0625 in thick.

TABLE 4. *Composition of residual product gases from a combustion experiment (mass spectrometric examination)*

Component	Mole percent
N_2	0.74
O_2	.87
CO_2	.16
CF_4	98.4
BF_3
SO_2F_2	0.008
SiF_4	.026
C_2F_6	.012
SF_6	.008

6. Calibration Experiments

Twenty calibration experiments were performed in which benzoic acid (Standard Sample 39i) was burned in 30 atm of oxygen and with 1 ml of distilled water in the nickel combustion bomb. Their consistency and reproducibility have been discussed in our earlier paper [11]. The average energy equivalent was calculated to be $14,803.27 \pm 0.99 \text{ J deg}^{-1}$. The uncertainty cited is the standard deviation of the mean. The energy equivalent is that of the standard initial oxygen calorimeter which included the nickel combustion bomb with 30 atm of oxygen, a platinum crucible and fuse support wires, platinum fuse (2 cm long, 0.01 cm diam), a type 304 stainless-steel liner, monel pellet holder, and no sample. Fastened to the bomb was a heater and ignition leads. The mass of the calorimeter vessel and water was 3750.0 g.

Using the appropriate heat capacity data, the energy equivalent of the standard oxygen calorimeter was adjusted to the proper value for the fluorine experiments. This involved allowing for the heat capacities of 30 atm of oxygen, 1 ml of distilled water, the platinum ware, 21 atm of fluorine, and two aluminum electrodes. The application of these corrections gave $14,805.17 \text{ J deg}^{-1}$ for the energy equivalent of the standard initial fluorine calorimeter over the temperature range used (27 to 30 $^{\circ}\text{C}$).

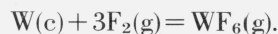
7. Fluorine Combustion Experiments

The calorimetric measurements included seven experiments, which have been previously reported in

detail [11], in which Teflon was burned in 21 atm of fluorine. The value listed in section 2.2 for the energy of combustion, ΔE_{303}° , was determined in these experiments. Ten heat measurements were performed in which boron-Teflon pellets were burned in 21 atm of fluorine. These measurements are summarized in table 5. In each experiment the sample pellet was placed in the recess of an "A" nickel plate on the bottom of the bomb. The bomb was attached to the fluorine manifold and filled to 21 atm with fluorine by the usual procedure. All bomb parts (bomb base, bomb-head assembly, electrodes, liner and nickel plate) were weighed before the first experiment and after each successive experiment. The bomb parts were washed with water and dried before the weighings were made.

The numbered entries in table 5 are as follows:

- (1a) Mass of the boron mixed with Teflon in the pellet, corrected for weight loss in preparation, for recovery of unburned boron, and for a boron blank.
- (1b) Mass of Teflon mixed with sample in the pellet, corrected for weight loss.
- (2) Pressure of fluorine introduced into the bomb prior to combustion, corrected to 30 $^{\circ}\text{C}$.
- (3) Energy equivalent of the initial calorimeter for a given experiment.
- (4) Temperature change of the calorimeter, corrected for heat of stirring and heat transfer.
- (5) Total energy change in the bomb process.
- (6) Energy liberated by the tungsten fuse assuming the fuse burns according to the reaction:



From the heat of formation of WF_6 [15], we calculate 9.44 J mg^{-1} for the energy of combustion of the fuse.

- (7) Net energy correction for the hypothetical compression and decompression of bomb gases.

$$\Delta E_{\text{gas}} = \Delta E^i(\text{gas})]_{P_0}^{P_i(\text{gas})} + \Delta E^f(\text{gas})]_{P_f}^0.$$

- (8) Standard energy of combustion per gram of Teflon at 30 $^{\circ}\text{C}$ multiplied by the corrected mass of Teflon in the pellet, (1b).

- (9) Standard energy of combustion per gram of the sample.

- (10) Average standard energy of combustion per gram of the sample.

- (11) Standard deviation of the mean of the average cited in (10).

- (12) Energy contribution by impurities.

- (13) Energy correction converting the reference temperature to 298 $^{\circ}\text{K}$.

- (14) Standard energy of combustion of the pure substance. Contributions from impurities have been accounted for both in mass and in energy.

- (15) ΔnRT term.

- (16) Standard heat of combustion at 298 $^{\circ}\text{K}$.

The heat capacities at constant pressure, C_p , used in the calculation of entries (3) and (13) are as follows in $\text{cal deg}^{-1} \text{ g}^{-1}$ at 25 $^{\circ}\text{C}$: boron, 0.245 [16]; and Teflon,

TABLE 5. Boron-Teflon combustion experiments

Experiment No.	1	2	3	4	5	6	7	8	9	10
(1a) m (sample).....g.....	0.157378	0.153795	0.151406	0.153477	0.163715	0.149249	0.152208	0.153996	0.160486	0.167872
(1b) m (Teflon).....g.....	2.767867	2.813748	2.675968	2.717357	2.880045	3.243633	3.168021	2.933396	3.053495	2.807121
(2) P (F ₂).....atm.....	21.2	21.6	21.4	21.6	21.4	21.8	21.6	21.9	22.0	21.9
(3) (e).....J deg ⁻¹	14,798.95	14,796.70	14,805.56	14,803.17	14,804.61	14,803.77	14,804.26	14,799.88	14,805.01	14,803.61
(4) ΔE ₂₉₈J.....	3.05494	3.06023	2.94249	2.98886	3.17645	3.33155	3.29647	3.14578	3.27706	3.15415
(5) (e) (-ΔE _c).....J.....	-45,209.9	-45,281.3	-43,565.2	-44,244.6	-47,026.1	-49,319.5	-48,801.8	-46,557.1	-48,516.9	-46,692.8
(6) ΔE ₂₉₈ (boron).....J.....	20.2	20.5	20.3	20.4	20.4	20.4	20.4	16.9	17.4	18.5
(7) ΔE ₂₉₈ (Teflon).....J.....	13.2	13.6	12.8	13.1	13.9	15.8	15.4	14.3	15.1	13.9
(8) ΔE ₂₉₈ (sample).....J.....	28,710.5	29,186.4	27,757.3	28,186.6	29,874.1	33,645.6	32,861.2	30,427.5	31,673.3	29,117.7
(9) ΔE ₂₉₈ (sample).....J.....	-104,627	-104,430	-104,189	-104,410	-104,558	-104,776	-104,494	-104,538	-104,731	-104,500

- (10) ΔE₂₉₈ (boron sample), Jg⁻¹ = -104,527 Jg⁻¹
 (11) Standard Deviation of the Mean = 54 Jg⁻¹ = 0.14 kcal mol⁻¹
 (12) Contribution from impurities = 545 Jg⁻¹ for 0.763 percent impurities
 (13) ΔE₂₉₈ - ΔE₂₉₈ = 2 Jg⁻¹
 (14) ΔE₂₉₈ (boron) = -104,779 Jg⁻¹ = -270.74 kcal mol⁻¹
 (15) ΔnRT = -115 Jg⁻¹
 (16) ΔH₂₉₈ (boron) = -104,894 Jg⁻¹ = -271.03 kcal mol⁻¹

0.28 [17]. The heat capacities at constant volume, C_v , used in the calculation of entries (3) and (13) were 5.52 [18], 12.62 [19], and 10.04 [16] cal deg⁻¹ mol⁻¹, respectively for fluorine, carbon tetrafluoride, and boron trifluoride at 30 °C.

Washburn corrections, entry (7), were calculated following the procedure outlined by Hubbard [20] for experiments in which fluorine is used as an oxidant. The coefficients $[\partial E/\partial P]_T = -T[dB/dT]$ were found in tables compiled by Hirschfelder, Curtiss and Bird [21] using the appropriate force constants. The force constants used for fluorine, carbon tetrafluoride, and boron trifluoride were those determined by White, Hu, and Johnston [22], Douslin [23], and Brooks and Raw [24], respectively. Force constants appropriate to the mixtures F₂, CF₄, and BF₃ in the reaction products were calculated from those for the pure components.

We assumed that the metallic impurities in the boron sample were present as the elements and that the non-metals, oxygen, nitrogen, and carbon were present as B₂O₃, BN, and B₄C, respectively.

In calculating the correction for the B₄C impurity in the boron sample, we have chosen $\Delta E_{298}^\circ = -97.84$ kJg⁻¹ for the reaction: B₄C(c) + 8F₂(g) = 4BF₃(g) + CF₄(g) based upon heat measurements performed in our laboratory. These latter data will be reported in more detail in a future publication.

Note that in adjusting the energy of combustion of the sample, entry (10), to the energy of combustion of pure boron, entry (14), the energy contributed by the impurities is subtracted from entry (10), and at the same time the mass of sample is reduced by the mass of the impurities. In calculating the corrections for the combustion of other impurities in the boron sample, the following heat of formation values were used and are given in kcal mol⁻¹: B₂O₃, -304.20 [25]; BN, -60.8 [25]; MgF₂, -268.7 [26]; CaF₂, -290.3 [27]; SiF₄, -385.98 [28]; FeF₃, -235 [29]; SrF₂, -290.3 [27]; MnF₃, -238 [29]; and AlF₃, -361.0 [11].

The raw data obtained in the benzoic acid calibration experiments were programmed for the IBM 7094 computer according to procedures outlined by Shomate [30] for the computer calculation of combustion bomb calorimetric data. The energy equivalent obtained was adjusted to that of the standard initial oxygen calorimeter as described in section 6. The combustion experiments were similarly programmed, however, the only valid data calculated by the computer were the corrected temperature rises, Δt_c , because the program used had not been modified to accommodate the use of fluorine as the oxidant.

Atomic weights were taken from the 1961 table of atomic weights based on ¹²C = 12 and adopted by the International Union of Pure and Applied Chemistry [31]. The unit of energy is the joule, and one calorie was defined as 4.1840 J.

About 500 mg of crystalline boron was transformed into boric acid solution by pyrohydrolysis³ and the solution examined by surface emission mass spec-

³ The authors are grateful to M. W. Lerner and L. J. Pinto, U.S.A.E.C. New Brunswick Laboratory, New Brunswick, New Jersey, for performing this task.

trometry⁴ for the isotopic abundance of B¹⁰/B¹¹. This study resulted in the atomic weight determination of our sample of 10.812 ± 0.005 . As a result of the good agreement with the atomic weight of boron in the table based on ¹²C=12 we have used the value 10.811 g mol⁻¹ from this table in our calculations.

8. Discussion and Results

A residue amounting to less than 1 mg which was assumed to be unburned Teflon and/or carbon, was observed in heat measurements involving Teflon alone. No correction was applied to any experiment for this residue, and we assumed that the formation of the residue took place in all experiments approximately in proportion to the amount of Teflon initially present. The heat of combustion per gram of Teflon would be constant and the error due to residue formation would be eliminated when the energy due to the combustion of Teflon in the pelleted mixture was subtracted from the total energy released in the combustion.

After a boron-Teflon combustion experiment, a larger residue was found than when only Teflon was burned, which necessitated determining the amount of unburned boron and also finding a method for gathering the residue from the nickel support plate. The mass of the residue was obtained by weighing the plate before and after the experiment. The average mass found from these weighings was 3 mg.

The residue was taken up from the support plate by mixing and rubbing Na₂CO₃ into the residue with a spatula. To determine the amount of boron, the residue mixed with Na₂CO₃ was fused and put into solution with dilute acid. The pH of the solution was adjusted, mannitol added, and the liberated acid titrated with base. The mass of unburned boron found in the residues by this analysis ranged from 0.5 to 1.1 mg. To determine the reliability of the above procedure, control experiments were performed in which crystalline boron was mixed with Na₂CO₃ and the mixture was analyzed for boron using the same procedure. As a result of the control experiments a correction factor was applied to the boron recovered from the residues. Analysis of residues mixed with Na₂CO₃ was made by the NBS Analysis and Purification Section.

We attempted to assign a composition to the residue even though the mass was subject to effects difficult to estimate such as reaction of the support plate with fluorine, hygroscopicity of the residue, and spattering of molten tungsten onto the plate from the ignition process. Our estimate for the boron blank, boron recovery, unburned Teflon, and tungsten account for about two thirds of the mass of the combustion residue. The remainder could be attributed to one of the above effects, but in the absence of definite information no adjustment was made for it.

A test made to determine whether the presence of boron affected the residue of Teflon, indicated a neg-

ligible effect. A boron-Teflon combustion residue was analyzed for carbon, and the results showed an amount comparable to the carbon content of residues formed from burning Teflon alone. A test for weight changes of pellets on exposure to fluorine indicated a slow weight increase, which was not fully reversed on evacuation. A pellet which has been exposed to fluorine and later exposed to moist air showed additional small weight gains, indicating a hygroscopicity resulting from the exposure to fluorine. These effects were small and slow, and no corrections were applied for them. However, they have been taken into account in assessing possible errors.

9. Summary of Errors

We have tried to estimate the overall experimental uncertainty for the heat of formation of BF₃(g) determined as a result of this investigation. Table 6 lists the errors considered in making the estimate. We have used the loss of sample found during the pelleting operation as a guide in estimating the error incurred in preparing a pellet (see table 3, line 6). From this source we estimate an error of 0.10 percent. The two oxygen analyses were 0.161 and 0.088 percent and the two carbon analyses were 0.05 and 0.11 percent. The effect that the differences of the analyses would have upon the heat data introduces an error of 0.06 percent.

TABLE 6. Summary of errors

Description of errors	Magnitude of error expressed in percent of ΔH_{298}° for boron
1. Weighing pellet.....	0.01
2. Loss during sample preparation.....	.10
3. Analysis of impurities.....	.06
4. Reaction prior to ignition.....	.03
5. Determining the amount of unburned boron.....	.06
6. Determining the composition of the combustion residue.....	.06
7. Fuse energy.....	.01
8. Bomb corrosion.....	.01
9. Calibration experiments.....	.01
10. Energy of combustion of Teflon [11].....	.03
11. Boron combustion experiments.....	.12
12. Atomic weight of boron.....	.05
13. Total error (percent).....	^a .19

^a (This is equivalent to 0.51 kcal mol⁻¹).

An error from the reaction of the sample in the bomb prior to ignition was estimated at 0.03 percent. This was based upon the assumption that prereaction occurring in the bomb prior to ignition was not more than 5 J hr⁻¹ as suggested by mass increments of pelleted mixtures upon exposure to fluorine. We assumed that the determination of unburned boron was not in error by more than 0.1 mg (0.06 percent) and that the additional error in estimating the total composition of the combustion residue is similarly 0.06 percent. Since the carbon in the boron combustion residue was comparable to the carbon from the combustion of Teflon alone, no error has been attributed to the uncertainty in residue left by the combustion of Teflon.

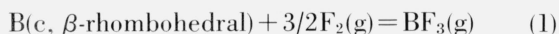
⁴ NBS Analysis and Purification Section.

Errors due to the weighing of the pellet, fuse energy, and bomb corrosion were estimated at 0.01 percent. Estimates of uncertainties arising from the benzoic acid calibration experiments, Teflon combustion experiments and combustions of boron-Teflon mixtures were made by multiplying the percent standard deviations of the means of the experiments by the appropriate factors for the Student *t* distribution at the 95 percent confidence level. Finally, we suggest that the error present in the determination of the atomic weight is 0.05 percent as a result of the experimental findings given in section 7.

The total percent error in this study was found by taking the square root of the sum of the squares of the individual errors cited.

10. Heat of Formation of Boron Trifluoride

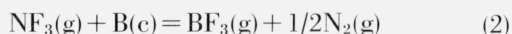
On the basis of the calorimetric data given in table 5, we calculate for the standard heat of reaction (1),



and, hence, the standard enthalpy of formation of boron trifluoride at 298 °K, -271.03 ± 0.14 kcal mol⁻¹. The latter uncertainty is the standard deviation of the mean. We estimate our overall experimental uncertainty to be 0.51 kcal mol⁻¹.

Our value for the enthalpy of formation of BF₃(g) is in good agreement with the result reported by Gross et al. [5], and differs from the result reported by Johnson et al. [6], by approximately our overall uncertainty.

Johnson et al. [6], have used some recent work by Gunn [32] on the solution of BF₃ in conc HF(aq), Good and Månsson [33] on the combustion of boron in oxygen in the presence of excess aqueous HF, their own data on $\Delta H_{f298}^\circ[\text{BF}_3(\text{g})]$, and other appropriate auxiliary data to derive a value for $\Delta H_{f298}^\circ[\text{HF} \cdot 3\text{H}_2\text{O}(\text{aq})] = -76.78$ kcal mol⁻¹. Insertion of our value for $\Delta H_{f298}^\circ[\text{BF}_3(\text{g})]$ into this cycle, gives -76.58 kcal mol⁻¹ for $\Delta H_{f298}^\circ[\text{HF} \cdot 3\text{H}_2\text{O}(\text{aq})]$. Both our work and that of Johnson et al. [6], agree in showing that the heats of formation for aqueous solutions of HF should be more negative than those suggested by Wagman et al. [34], but less negative than those indicated by Cox and Harrop [35]. In this respect they substantiate our similar finding on the heat of formation of HF(aq) as derived from several other reactions in our study of the heat of formation of CF₄ [11]. Ludwig and Cooper [36] reported for the heat of reaction (2),



$\Delta H_{298}^\circ = -239.7 \pm 1.2$ kcal mol⁻¹. Combining our data on $\Delta H_{f298}^\circ[\text{BF}_3(\text{g})]$ with the heat of reaction (2), we calculate for $\Delta H_{f298}^\circ[\text{NF}_3(\text{g})]$, -31.33 kcal mol⁻¹. Although this is in good agreement with the heat of formation of NF₃(g), -31.44 kcal mol⁻¹ reported by Sinke [37], the merits of the agreement are dubious because of the large uncertainty associated with the heat of reaction (2).

11. References

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